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TITLE NTO DEVELOPMENT AT LOS ALAMOS

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NTO DEVELOPMENT AT LOS ALAMOS

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NTO is an explosive with calculated performance near that of RDX but with sensitivity approaching that of TATB. Possible uses for NTO would be as an alternative to RDX in formulations where a lower sensitivity is desired or as an alternative to TATB where more performance is required without a large increase in sensitivity. Efforts have been concentrated on producing NTO and in testing the performance and sensitivity of NTO and NTO formulations. Two hundred pounds of NTO have been produced and some performance and sensitivity data have been obtained. Work is being done to determine the diameter effect for large crystal size NTO. Additional work is being done to improve the small charge diameter performance of NTO by adding small amounts of RDX or by changing the crystal size and/or crystal habit of the NTO.

INTRODUCTION

A new molecule, 3 nitro 1,2,4 triazole 5 one (NTO), was found in the literature[1] without reference to its energetic properties. NTO was first recognized as a potential explosive molecule and then synthesized by K. Y. Lee and M. D. Coburn[2] at Los Alamos. Small scale sensitivity and thermal tests indicated that NTO was a very impact insensitive and thermally stable molecule. Preliminary performance calculations also indicated that the performance of NTO would be near that of RDX. Based upon this preliminary information, NTO was synthesized and tested in small scale at Los Alamos. The performance of NTO in these small scale tests was not as good as the preliminary calculations indicated it should be, therefore larger quantities were required for more extensive performance and sensitivity tests as well as for development of NTO formulations that might be useful in both DOE and DoD applications.

NTO SCALE UP AND PRODUCTION

NTO production begins by producing the intermediate, 1,2,4 triazole 5 one (TO). TO is made by reacting semicarbazide HCl with 90% formic acid at 90 to 100°C. NMR studies by Don Ott[3] have shown that the reaction to TO is essentially complete when the HCl gas evolution stops and there is no need for extended reaction times. It was also determined that some HCl is needed to complete the reaction and that semicarbazide alone without the HCl stabilizer does not produce ring closure to form TO. TO batch production has been scaled up to a 40 gal reactor with recovered product weight of 16.62 kg at a 73.8% yield.

NTO reaction yield has averaged 76% when a mixture of nitric and sulfuric acid is used to nitrate TO. The highest yield (87.5%) was obtained when the acid mixture was first added to the reactor and brought to 60 70°C. The acid mixture contains an 85/15 ratio of nitric to sulfuric acid (the nitric acid concentration used is 70% while the sulfuric acid is 96%). TO was then added slowly, after the acid reached reaction temperature.

NTO was produced in 5 kg batches with a total recrystallized production of 47.7 kg (104.9 lb). Three 15 kg batches have also been produced but have not been recrystallized.

TOXICOLOGICAL STUDIES ON NTO AND TO

Toxicological studies have been done for both NTO[4] and the production intermediate TO.[5] Results of the tests indicate that neither NTO nor TO present concerns of acute toxicity, skin irritation, skin sensitization, and eye irritation. In fact, the acute oral LD 50 for both NTO and TO is greater than 5 g/kg in rats and mice, which is considered only mildly or not toxic in both species.

DEPARTMENT OF TRANSPORTATION CLASSIFICATION TESTS

Thermal stability and sensitivity tests were done at Los Alamos in order to apply for a D.O.T. shipping hazard classification. A heating test was conducted for 48 hours at 75°C and produced no evidence of decomposition or discoloration. Two ignition and unconfined burns were done with a single sample 2 x 2 x 2 in. and another was done with four samples end to end. There was no detonation and burn times exceeded 300 seconds. Impact sensitivity for large particle-size NTO is much less than RDX and near the height limits of the Los Alamos drop weight impact machine. The shock sensitivity was tested by a confined-gap test and results were comparable to PBX 9502 in the same test. A sample of bulk NTO was detonated with a number 6 blasting cap.

Based upon the results of these tests, NTO fits the criteria for a Class A explosive. NTO has not received a permanent D.O.T. classification at this time.

HIGH-SPEED-MACHINING TEST

Pure, pressed NTO and NTO cast with 50 wt% TNT have undergone high-speed-machining tests. The standard test is performed by drilling 40 0.250-in. diam holes into an explosive charge. The drill speed is 2260 RPM and the penetration rate is 0.025 in. per revolution. NTO is soluble in water and was, therefore, machined dry. Both samples produced no reaction during testing and were approved for remote control machining operations.

NTO PERFORMANCE

NTO CYLINDER TESTS

Two inch diameter NTO charges were pressed at 1.855, 1.825, and 1.800 g/cm^3. The diameters were machined to fit into 2 in. diam copper cylinders for cylinder expansion tests. Two of the three charges were fired successfully indicating NTO has a performance greater than TATB.

CONFINED NTO PLATE DENT/DETONATION VELOCITIES

Several plate dent tests were made with explosives of known performance to try and calibrate a confined plate dent test. The explosives were confined in schedule 80 steel pipe with an inner diameter machined to accept 1-5/8 in. pressed charges. NTO was also tested in the same manner to determine if confinement would improve its performance in smaller diameters. The preliminary measured velocities are shown in Table 1 along with calculated values. Additional tests were done with NTO pressed to 97% TMD (1.871 g/cm^3) in both confined and unconfined modes for comparison. The detonation velocities are obtained from piezoelectric pins in contact with the HE surface and are for screening only. These results indicate that there is a diameter effect present in NTO fired in 1-5/8-in. diam at high densities.

TABLE 1. PERFORMANCE COMPARISONS

	Calculated (unconfined)		Measured
Density (g/cm^3)	Pres. (kbar)	Vel. (km/s)	Det.Vel. (km/s)
1.93 (100% TMD)	340	8.67	
1.871 (97% TMD)	--		8.22 confined
1.871 (97% TMD)	-	--	8.12 unconfined
1.855 (96.1% TMD)	306	8.34	8.20 confined
1.825 (94.6% TMD)	294	8.21	8.09 confined
1.800 (93.3% TMD)	283	8.11	8.02 confined

NTO FAILURE DIAMETER AND DIAMETER EFFECT

Experiments were performed by Ray Engelke[6] to determine diameter effects and failure diameter of large crystal size NTO (Blend 87-10). The first NTO charges were pressed to 1.868 g/cm^3 (96.8% TMD) and machined down to 36 mm diam. A 36-mm-diam rate stick was fired and propagated at 8.176+/-0.001 km/s. A second rate stick was fired that included three different diameters; 32.5, 28.9, and 25.35 mm. A third rate stick was set up with 25.4, 19.1, and 16.7-mm diameter NTO charges arranged from large to small diameter following the booster. This failed in the 25.4 mm diameter section.

Rate sticks are normally initiated using an RP-1 detonator with a 1/2 in. diam by 1/2 in. high PBX 9407 booster pellet. This booster pellet then initiates a PBX 9404 charge that is at least as large in diameter as the largest diameter test charge. A fourth NTO rate stick was assembled with an NTO charge 25.76 mm diam, using a booster consisting of a P22 plane wave lens followed by a 0.25 in. thick by 2 in. diam PBX 9404 charge. This rate stick propagated its entire length with a steady velocity. Detonation velocity results are shown in Table 2. These results indicate the failure diameter of large crystal size NTO at this density is near one inch.

NTO/BINDER FORMULATIONS

NTO/binder formulations in 95/5 wt% concentrations were tested in 5 g slurry batch sizes to determine compatibility before further scale up. FPC 461, Viton A, Kel F 800, Estane, and Kraton G were evaluated for possible binders. None of the NTO/binder combinations showed evidence of incompatibility. All of the binders produced a formulation that was less impact sensitive than the pure NTO. Ethyl acetate was chosen over MEK as a solvent because it produced a better attraction between the lacquer and the explosive. Because NTO is soluble in hot water, a saturated NTO solution at 55°C was used as the carrier instead of pure water. NTO was mixed

TABLE 2. NTO BLEND 87 10 DETONATION VELOCITY

Diameter (mm)	Det. Vel. (km/s)	Density (g/cm^3)
36.00	8.176 +/-0.001	1.868
32.51	8.160 +/-0.001	1.870
28.91	8.159 +/-0.004	1.869
25.35	8.144 +/-0.001	1.867
25.40	Failed	1.868
25.76	8.142 +/-0.005	1.870

with the lacquer to provide intimate contact and wetting of the NTO crystals before the water was added. Based upon high binder density and the higher bulk densities obtained in the initial 5-g-scale work, four binders were chosen for scale up to 50-g batches. Kraton G did not produce an acceptable formulation. As was found in the 5 g scale batches, FPC-461 produced the best agglomerates with a bulk density of 0.7 - 0.75 g/cm^3. Based upon small scale results, FPC 461 was used to make a one kilogram batch of X 0483* by the water-slurry method.

NTO/TNT CASTINGS

X 0489** was cast in one 4 in. diam x 6 in. high cylinder and in eight 1 5/8 in. diam x 4 in.-high cylinders. All the charges were radiographed and showed minimal shrinkage and bubbles. Vacuum was not applied to the melt but the castings were cooled from the bottom to the top. A casting sample was taken for thermal stability and impact sensitivity testing and a release has been issued for this batch. The 4 in. diam x 5 in. high cylinder was used for a high speed machining test. After the material passed the machining test, the casting risers were removed from the 1 5/8 in. charges, which were then fired in a combination plate dent/rate stick to determine the performance of the X 0489. The results are shown in Table 3, along with a calculated performance for comparison.

TABLE 3 PERFORMANCE OF X 0489 CASTINGS

Stick Number	Density (g/cm^3)	Pressure (kbar)	Det. Vel. (km/s)
1	1.711	240	no data
2	1.717	241	7.226 +/ 0.011
3	1.720	242	7.225 +/ 0.008
Calculated	1.720	246	7.56

* X 0483 95/5 wt% NTO/FPC 461
**X 0489 50/50 wt% NTO/TNT

NTO RECRYSTALLIZATION

INTRODUCTION

Normally NTO is recrystallized from hot water after initial production to remove entrapped nitric acid. A mean particle size of 250 microns, shown in Figure 1, is obtained by the normal recrystallization method of cooling the entire vessel and contents from 90 to 5°C over a 30-minute period. A smaller particle size was desired for PBX formulations work and to determine the effect of smaller particles on performance, sensitivity, and failure diameter. Preliminary results indicate that impact sensitivity and performance do change with particle/crystal size distribution.

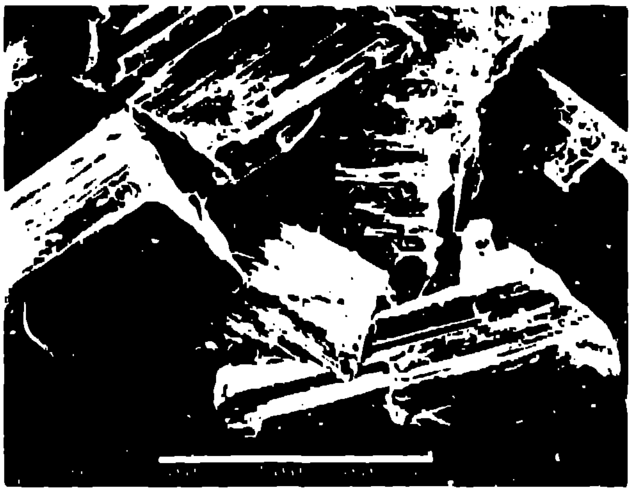

FIGURE 1. NTO RECRYSTALLIZED SLOWLY FROM WATER

NTO RECRYSTALLIZATION FROM WATER

Work was done to reduce NTO particle size by crash precipitating a saturated NTO/water solution at 91°C into ice water. The melting ice maintained the recrystallization temperature between 0 and 5°C. Particle size in this batch (LBC 111 78) averaged about 40 microns. SEM photographs in Figure 2 show that the NTO clumps are made up of 5 to 25 micron crystals. These clumps are smaller and are more randomly arranged than previous precipitations done at 5 to 20°C.

NTO BATCH RECRYSTALLIZATION FROM NMP

Particle/crystal size were reduced further by dissolving NTO into N methyl pyrrolidone (NMP) in a 65 g/100 g concentration at 90°C. This

FIGURE 2. NTO CRASH PRECIPITATED FROM WATER

FIGURE 3. NTO RECRYSTALLIZED FROM NMP, RANDOM GROWTH

solution was poured into ice water with agitation and with ice being added to maintain the temperature below 5°C. Batch LBC 111 6C, shown in Figure 3, was made using this procedure. This SEM photograph shows 50 to 100 micron "clumps" that contain many 2 to 10 micron crystals, but the crystals are randomly packed and look like they contain a large amount of voids.

NTO dissolved in NMP and crashed into ice water can produce spherical crystal growth that is similar to spherical NQ produced at Los Alamos. The crystal size produced with a 1:1 ratio of H_2O:NMP, shown in Figure 4, is very small (i.e., 1-5 microns) and is in spheres ranging from 10 to 30 microns in diameter. Individual crystal size can be controlled by changing the ratio of ice water to NMP/NTO solution. Agglomerates containing a random arrangement of small crystals can be obtained by adding additional NMP/NTO solution to the combined solutions after crystal formation has begun.

FIGURE 4. NTO RECRYSTALLIZED FROM NMP, SPHERICAL GROWTH

Small crystal size (i.e., 1-10 micron) spherical NTO produced by batch recrystallization from NMP was pressed into 1/2 in. diam pellets for plate dent comparison with previously produced NTO. Plate dent results for Batch 111 222, shown in Figure 5, were 263 kbar at 1.764 g/cm³ (91.4% TMD) and 257 kbar at 1.827 g/cm³ (94.7% TMD). Drop weight impact sensitivity is about 200 cm for this small crystal size material. These results are not significantly different from other small crystal size NTO, which indicates that spherical crystal habit does not seem to be as important as individual crystal size in reducing failure diameter.

Plate dent results shown in Figure 5, indicate the performance of Batch LBC 111 6C (designated 6C) is close to the BKW prediction while the other small particle size batches (designated 7A and 222) perform better than the large particle size NTO at the same density. Previous unconfined plate dents using large particle size NTO in 1/2 and 1 in. diam failed to propagate at densities greater than 1.59 g/cm³. Also 1/2 in. diam plate dents using NTO Blend 87 10 failed to propagate at 1.78 and 1.72 g/cm³. Unconfined 1 5/8 in. diam plate dents using large particle size NTO have propagated at densities up to 1.827 g/cm³ but the performance, shown in Figure 5, is lower than expected and begins to drop with increasing density at 1.855 g/cm^3. These results show that smaller particle sizes can improve NTO performance in small diameters and might perform close to BKW predictions at higher densities in larger diameters.

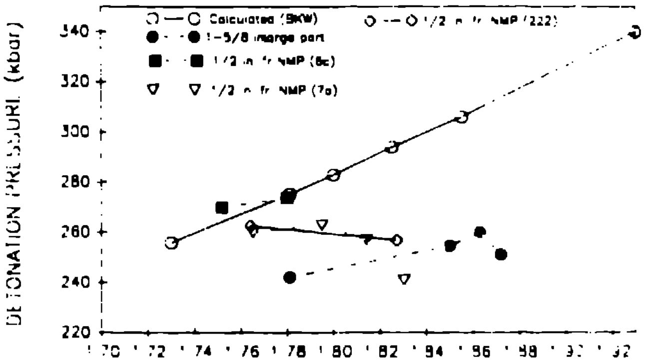

FIGURE 5. CHARGE DENSITY (g/cm^3)

NTO CONTINUOUS RECRYSTALLIZATION FROM NMP

Equipment for continuous, single vessel recrystallization was tested at a rate that would produce 800 g/h of NTO at 99% yield. The NTO/NMP solution is first cooled to room temperature before mixing with the water to reduce the amount of heat exchange required. NTO/NMP remains a stable solution for several hours at room temperature in the concentration used. The coolant temperature was increased from 12 to 5°C and a distilled water flush was installed to reduce heat exchanger plugging.

A new recrystallization vessel is being made to allow flow patterns approaching plug flow and to provide capacity for increased flow rates. The new vessel is jacketed to provide cooling to replace the double pipe heat exchanger that is currently causing plugging problems.

NTO/RDX/BINDER FORMULATIONS

PBXs using mixtures of NTO and RDX are being prepared in an attempt to reduce the failure diameter of NTO formulations. The failure diameter as a function of RDX content will be investigated. PBXs containing both NTO and RDX were successfully made with good agglomerate size and strength. Impact sensitivity and thermal analysis data for these PBXs indicate there is no incompatibility between NTO, RDX, and these binders.

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